

FIBER-REINFORCED COMPOSITE CERAMIC, FABRICATION METHOD AND  
LINING MATERIAL, ARMOR, REFLECTIVE SURFACE AND COMPONENT  
HAVING THE COMPOSITE CERAMIC

Background of the Invention:

Field of the Invention:

The invention relates to fiber-reinforced composite ceramic  
 with a matrix containing silicon carbide (SiC) and/or silicon  
 (Si). The invention also relates to a method for fabrication  
 of the composite ceramic. The invention additionally relates  
 to lining material, armor, reflective surfaces and components  
 having the composite ceramic.

German Published, Non-Prosecuted Patent Application DE 197 10  
 105 A1, corresponding to U.S. Patent No. 6,030,913, describes  
 a composite ceramic that is reinforced with high-tenacity  
 graphite short fibers. The ceramic has a matrix substantially  
 formed of SiC, in other words a C/SiC material. The matrix of  
 the ceramic composite material is formed substantially through  
 the use of the liquid silication of a carbon prebody with a  
 silicon melt. The reinforcing short fibers are surrounded by  
 at least two sheathes formed of graphited carbon, which is  
 formed by carbonizing and graphiting impregnation agents,  
 particularly synthetic resin or pitch. At least the outermost

sheathe thereof is converted into silicon carbide by reaction with liquid silicon. The fiber bundles that are utilized for reinforcement are obtained by compressing fiber prepregs at least once with a carbonizable impregnating agent, carbonizing  
5 and graphiting them, and then milling them into short-fiber bundles. The milled fiber bundles are mixed with fillers and binders and pressed into green bodies, which are then carbonized and infiltrated with liquid silicon. The resulting composite material exhibits a quasi-ductile fracture behavior  
10 with an elongation at break of approximately 0.25 to 0.5%. The density of the composite material equals  $2.27 \text{ g/cm}^3$ .

When using the known method, it is impossible to increase the density significantly through the use of increased SiC  
15 formation, without substantially reducing the elongation at break. However, for a series of applications, a high density (i.e. a low porosity) and high elongation at break (or tenacity behavior) of the C/SiC material are critical. For instance, low porosity and high ceramic content are important  
20 when utilizing composite materials for ballistic protection, for instance as flak plates, in order to achieve a shot refracting effect. At the same time, a high elongation at break is desirable for the material in order to prevent brittle fractures when the projectiles hit. Besides that, a  
25 low porosity (high density) plays an important role in high-

temperature applications, because air can reach the carbon fibers through open pores and cause oxidation damage.

Summary of the Invention:

5 It is accordingly an object of the invention to provide a fiber-reinforced composite ceramic, a fabrication method and a lining material, an armor, a reflective surface and a component having the composite ceramic, which overcome the hereinafore-mentioned disadvantages of the heretofore-known  
10 products and methods of this general type and in which the composite material exhibits a high tenacity in addition to its high density.

With the foregoing and other objects in view there is  
15 provided, in accordance with the invention, a fiber-reinforced composite ceramic, comprising a matrix containing SiC and/or Si. A density of greater than  $2.5 \text{ g/cm}^3$  and an elongation at break of greater than 0.3% are provided.

20 With the objects of the invention in view, there is also provided a method for producing fiber-reinforced composite ceramic, which comprises providing a matrix containing SiC and/or Si in a step a). A blend containing carbon fibers, carbonizable bonding resin, and additional carbon material  
25 having a raw density in a range of  $0.7$  to  $1.8 \text{ g/cm}^3$  is produced in a step b). The blend is molded or pressed into a fiber-

reinforced green body in a step c). The green body is carbonized to produce a C/C body in a step d). The C/C body is infiltrated with a silicon melt in a step e).

- 5 Raw density means the geometric density derivable by measuring the mass of a precise sample volume. Density as used below refers to raw density.

The method for fabricating the carbon-fiber-reinforced SiC ceramic composite material with high density and a high elongation at break includes, first, according to step b), the fabricating of a pressable blend containing carbon fibers, particularly carbon fiber bundles, carbonizable bonding resin and additional carbon material.

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The carbon fiber bundles are preferably formed by layered carbon short fibers, which are typically held together in bundles by polymer or carbon.

- 20 Phenol or furfuryl alcohol resins are preferably used as the carbonizable bonding resin.

Unprotected fiber material, graphite, carbonized bonding agents, carbonization residue, or the like, are preferably used as the additional carbon material. The purpose of the additional carbon material is to convert into SiC as a

"sacrificial material" at the outset of the silicon melt infiltration. A high SiC yield is the object of the liquid silication process. Prior attempts to achieve high composite material densities were based on the assumption that the carbon material must include the highest possible carbon content, such as graphite, for instance, in order to be able to develop as much SiC as possible.

However, experiments conducted by the applicant of the instant application have shown that natural graphite cannot be added in sufficient quantities to generate a body with high density. The sharp volume increase of the reaction product relative to the starting substances Si and C that is associated with the reaction of natural graphite into SiC would lead to swelling or exploding of the composite material body given larger graphite quantities. That is because a sharp volume increase of approximately 135% occurs in the reaction between natural graphite and silicon into SiC. With higher graphite quantities, that behavior can lead to a change in geometry or even destruction of the molding body.

It was observed that, besides its chemical reactivity, the density of the carbon material in the C/C body that is provided for silicon melt infiltration is specifically responsible for the density of the SiC matrix that is formed therefrom and the residual porosity of the ceramic composite

material. It was determined that the conversion of the carbon material by the liquid silication leads to dense SiC, and the filling of the residual porosity of the C/SiC body it forms, only when the density of the carbon material is within defined limits. Additional carbon material with an average density in a range from 0.7 to 1.8 g/cm<sup>3</sup>, preferably from 0.7 to 1.6 g/cm<sup>3</sup> and particularly from 0.7 to 1.3 g/cm<sup>3</sup>, is added to the pressable blend, according to the invention. The density of the suitable carbon material is thus appreciably below the density of natural graphite (2.25 g/cm<sup>3</sup>). The utilization of a carbon material with a density within the range according to the invention also guarantees that the conversion into SiC does not lead to a volume increase that would damage the composite material.

Expanded graphite, preferably following an intermediate compressing process, has a density within the cited range. Another advantage of expanded graphite is its high reactivity in relation to the silicon melt, which leads to uniform silication and short reaction time. The expanded graphite is obtained by the thermal decomposition of a graphite-intercalation product. Compounds based on graphite/sulfuric acid, graphite/nitric acid, or graphite/perchloric acid are particularly relevant in this regard. Expanded graphite is also obtained in the form of a loose vermiform substance from the short-term heating of graphite salts or graphite inclusion

compounds such as graphite hydrogen sulfates or graphite nitrates or graphite perchlorates, as described in European Patent Application EP 1 120 378 A2, corresponding to U.S. Patent Application Publication No. US 2001/0018040 A1, for  
5 example. Graphite films or plates can be generated by compressing the expanded graphite. These films or plates of expanded graphite have a raw density between 0.7 and 1.8 g/cm<sup>3</sup>. An expanded graphite powder can be produced which processes well and which can be mixed into molding materials  
10 homogenously in a dispersed fashion, by pulverizing the precompressed expanded graphite with the aid of a cutting mill, impact mill, or jet mill. The raw density of the crushed powder generally only negligibly deviates from that of the graphite films.

15 The crushed powder of precompressed expanded graphite typically has a bulk density between 0.04 and 0.18 g/cm<sup>3</sup>. A powder with a bulk density between 0.05 and 0.14, and particularly between 0.06 and 0.1 g/cm<sup>3</sup>, is preferred.

20 In contrast, uncompressed and unmilled powder of expanded graphite generally has a substantially lower bulk density of approximately 0.002 to 0.008 g/cm<sup>3</sup>. That low density makes processing subsequent to the cited process for fabricating  
25 composite ceramics extraordinarily difficult.

Besides the density of the material, the particle size and morphology of the additional carbon material are also important. In particular, fiber-shaped or platelet-shaped reinforcing materials lead to high reinforcing effects in composite materials. In a preferred development of the invention, a platelet-shaped carbon material is used. It is preferably formed from expanded graphite. Expanded graphite that has been precompressed to a density of approximately 1 g/cm<sup>3</sup> is particularly preferred. The precompression can be achieved by pressing the graphite into films, for example. For their part, the graphite films can be easily crushed to a defined particle size. The platelet-shaped particles having a height/diameter ratio of over 50, preferably over 80, and particularly over 120, are preferred. The morphology of the preferred platelet-shaped carbon particles with a density of approximately 1 g/cm<sup>3</sup> is represented in Fig. 1.

Beyond that, the additional carbon material can also have a fiber-shaped configuration. Specifically, carbon nanotubes are fiber-shaped carbon materials with a suitable density and reactivity.

The suitable average particle size of the carbon material, particularly the platelet material, is under 500  $\mu\text{m}$ , preferably in a range between 0.1 and 300  $\mu\text{m}$ , and particularly



in a range between 0.1 and 100  $\mu\text{m}$ . Particle size refers to the agglomeration-free primary particle. The mass % of carbon material is advantageously less than 45% in the moldable blend. Mass percents in the range between 2 and 35% are particularly preferred.

The molding of the moldable material according to step c) usually occurs in a press, with it being possible to cure the material thermally or catalytically. Other pressure molding methods can also be used, depending on the consistency of the material. The addition of expanded graphite, in particular, leads to a relatively good sliding and flowing capability, so that injection molding or related molding techniques can also be carried out.

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In step d), the resulting green body is baked (i.e. carbonized) at temperatures between 750 and 1200° C in the absence of air in order to produce the carbonaceous porous prebody (C/C body). During this process, the bonding resin is broken down into carbon. The carbonization may also be carried out at temperatures near 2400° C. At these temperatures, the graphiting of carbon that has not yet been graphited occurs.

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In the final step e), the C/C body is infiltrated with a silicon melt according to the conventional technique,

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preferably through the use of wicks. At least part of the carbon of the C/C body is converted into SiC. A ceramic composite material with a matrix composed predominantly of SiC is thereby formed. Residual silicon and residual carbon occur  
5 in the ceramic composite material as additional matrix components. When expanded graphite is used as the preferred added carbon material, a relatively low residual silicon content can be set. The proportion of free silicon (residual silicon) in the ceramic composite material according to the  
10 invention is thus advantageously under 10% by mass. In the case of an application as an anti-ballistic material or as a component of armor plating, the mass % of Si is preferably set at less than 7%. High SiC contents can be achieved in correspondence to the low residual silicon content. The  
15 proportion of SiC in the ceramic composite material is advantageously more than 60 % by mass. A high SiC content is important particularly in anti-ballistic applications. In this case, the proportion of SiC is preferably above 70% by mass.

20 Beyond this, other metals besides silicon can be present in the silicon melt that is provided for the infiltration, such as Fe, Cr, W or Mo, the proportion of which in the melt typically does not exceed 20%. Ti is particularly preferred  
25 as an additional carbide forming metal. Silicon is also characterized as a metal in the context of this application.

The ceramic composite material that is produced with the method according to the invention has a density of over 2.5 g/cm<sup>3</sup>. This value refers to infiltration with pure silicon.

- 5 When silicon alloys containing metals of greater or lesser density than silicon are used, these density ranges must be adapted according to the theoretical values. The open porosity of the fiber-reinforced ceramic composite material is under 5% and the elongation at break is greater than 0.3%.
- 10 The composite material that is produced by the method according to the invention thus advantageously combines a high material density (i.e. low porosity) with a relatively high elongation at break.
- 15 The composite material is particularly well suited for thermally loaded components under oxidizing or corrosive conditions by virtue of the high density (low porosity). The low porosity prevents air from diffusing in and causing oxidative damage to the carbon reinforcing fibers. Typical
- 20 fields of application are thus linings for combustion chambers or furnaces.

Another application of the fiber-reinforced composite ceramic according to the invention is in the field of armor materials.

- 25 It is known that ceramic materials make good plating materials for armor and for protection against projectiles. More

specifically, the high material density of the composite material that is produced by the method according to the invention results in a favorable refracting effect. Material densities above  $2.6 \text{ g/cm}^3$  are preferred for anti-ballistic applications. The fiber-reinforced ceramics according to the invention have a substantially higher fracture toughness as compared to monolithic ceramics.

A further application advantageously exploits the good polishability of the composite material surfaces that comes from the high material density. This permits the ceramic composite material to be used in the fabrication of mirrors in lightweight structures, particularly satellite mirrors. The mirror surfaces then need not be coated with high-polishing glasses or silicon in the customary manner.

The invention can also be applied to components for precision machines and calibration bodies. In this case, the very small and uniform thermal expansion of the composite material according to the invention across a large temperature range is of critical importance. Due to its high stability, rigidity, and wear resistance, the composite material can also be used directly as a structural element of heavily loaded machine components.

Other features which are considered as characteristic for the invention are set forth in the appended claims.

Although the invention is illustrated and described herein as embodied in a fiber-reinforced composite ceramic, a  
5 fabrication method and a lining material, an armor, a reflective surface and a component having the composite ceramic, it is nevertheless not intended to be limited to the details shown, since various modifications and structural  
10 changes may be made therein without departing from the spirit of the invention and within the scope and range of equivalents of the claims.

The construction and method of operation of the invention,  
15 however, together with additional objects and advantages thereof will be best understood from the following description of specific embodiments when read in connection with the following examples and accompanying drawings.

20 Table 1 represents mechanical characteristics such as ultimate breaking strength, elongation at break, and density of composite ceramics (specimens PF 413, 414, 450, 460) produced according to the invention in comparison with a composite ceramic that was produced by another method (specimens PF 420,  
25 444), as a function of the starting substances that were used in the blend and the quantities thereof.

Carbon-coated short-fiber bundles, bonding resin in the form of phenol resin, and expanded graphite with a density of approximately  $1 \text{ g/cm}^3$  were utilized as the additional carbon material for producing the blend in specimens PF 413, 414, 450 and 460, respectively. The specimens differ with respect to the quantity of carbon-coated short-fiber bundles, carbon fibers, expanded graphite and bonding resin. The different types of short-fiber bundles (Type A and Type B) differ only in the filament number and morphology of the fiber strands that are used to make the fiber bundle.

The specimens PF 420 and 444 were produced with natural graphite with a density of  $2.25 \text{ g/cm}^3$ . Like the specimens produced according to the method according to the invention, carbon-coated short-fiber bundles were utilized in these specimens as well.

The results show that, with the addition of expanded graphite, there is an increase in the density of the composite material from  $2.26 \text{ g/cm}^3$  to  $2.75 \text{ g/cm}^3$  relative to the control specimen PF 420 (5% natural graphite, 47% phenol resin), without a reduction in elongation at break or ultimate breaking strength. The control specimen PF 444 shows that these results cannot be achieved with the substantially denser natural graphite ( $2.25 \text{ g/cm}^3$ ). The specimens of the test

series PF 444, which contain 10% natural graphite, were sharply swollen and in part completely destroyed by the reaction of the graphite into SiC.

5            Table 1: Mechanical Characteristics of Specimens in Dependence on Type and Amount of Starting Substance

Specimen No. PF...	Carbon Fiber	Carbon Material	Proportion of Carbon Material (%)	Density Carbon Material (g/cm <sup>3</sup> )	Proportion of Phenol Resin (%)	Ultimate Breaking Strength (MPa)	Elongation at Break (%)	Density (g/cm <sup>3</sup> )
413	Type A 48%	Expanded graphite	4	1	48	44	0.25	2.56
414	Type A 50%	Expanded graphite	10	1	40	55	0.3	2.52
450	Type B 60%	Expanded graphite	10	1	30			2.60
460	Type B 55%	Expanded graphite	15	1	30			2.75
444	Type A 50%	Natural graphite	10	2.25	40	Specimen body swelled and destroyed		

#### Brief Description of the Drawings:

Fig. 1 is a raster electron microscopy image of platelet-shaped carbon particles with a density of approx. 1 g/cm<sup>3</sup>;

Fig. 2 is a micrograph of a control specimen without an addition of carbon material, representing regions of silicon carbide, silicon, carbon fibers, and pores; and

Fig. 3 shows a specimen PF 460, which is produced with expanded graphite.

#### Description of the Preferred Embodiments:

Referring now to the figures of the drawings in detail and first, particularly, to Fig. 2 thereof, there is seen a

micrograph which shows regions of silicon carbide 1, silicon  
2, carbon fibers 3 and pores 4.

The influence of the expanded graphite is evident particularly  
5 from a comparison of the microstructure (represented as a  
micrograph) of the C/SiC ceramics with a graphite addition to  
those without the addition of carbon material. Besides  
showing phases of SiC 1 and carbon fibers or fiber bundles 3,  
the control specimen in Fig. 2, in which no carbon material  
10 whatsoever was added, shows relatively large regions of Si  
phases 2 or pores 4, both of which are undesirable with  
respect to the required material characteristics.

In contrast, the specimen PF 460 with an addition of 15%  
15 expanded graphite shown in Fig. 3 still exhibits only very  
small regions with Si phases 2. Furthermore, the number of  
pores 4 as well as their cross-sectional area are  
substantially reduced. The carbon fiber bundles are  
advantageously completely surrounded by a dense SiC matrix  
20 almost without exception.